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2005 Progress Report for Grant #F49620-02-1-0312

**Fluorescence Enhancement Under Controlled Electromagnetic
Nanoenvironments**

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2. Objectives (as stated in proposal abstract): In the proposed project we are investigating the role of the electromagnetic nanoenvironment on fundamental photophysical processes in molecular and ionic optically active species. Both nanoshells and nanopatterned surfaces are being used to apply specific and controlled local field enhancements to chromophores of interest. These structures are designed and analyzed using finite-difference time domain and Mie scattering methods to ensure close correspondence between the predicted and actual fields at the nanostructure. By detuning the plasmon resonance at or near a molecular or ionic resonance, the effect of the local field on specific, selected energy transitions within a chromophore can be studied. Changes in spontaneous emission rates due to the modified photon density of states resulting from confined geometries are also to be addressed.

Specifically, we will investigate changes in single and multiphoton absorption and fluorescence in the spectral and time domains in molecular and rare earth optically active species; modifications in triplet state lifetime in molecular species; and enhancements of one and two-photon absorption when the plasmon resonance is tuned to the single photon virtual level.

The scientific and technological relevance of these investigations is extremely significant. Developing a more detailed understanding of energy transfer under controlled electromagnetic nanoenvironments can enable us to ultimately "design" new optical and photonic media and devices with optimized properties: lower threshold lasers, photonic devices and waveguides in new compact geometries and sizes consistent with the ongoing miniaturization of electronic components, new strategies in optimizing the efficiency of detectors, improved design of optical interconnects for enhanced response and performance, new types of optoelectronic devices. The new level of understanding resulting from these investigations will likely provide revolutionary new strategies for tailoring light-matter interactions using intelligently designed nanostructures.

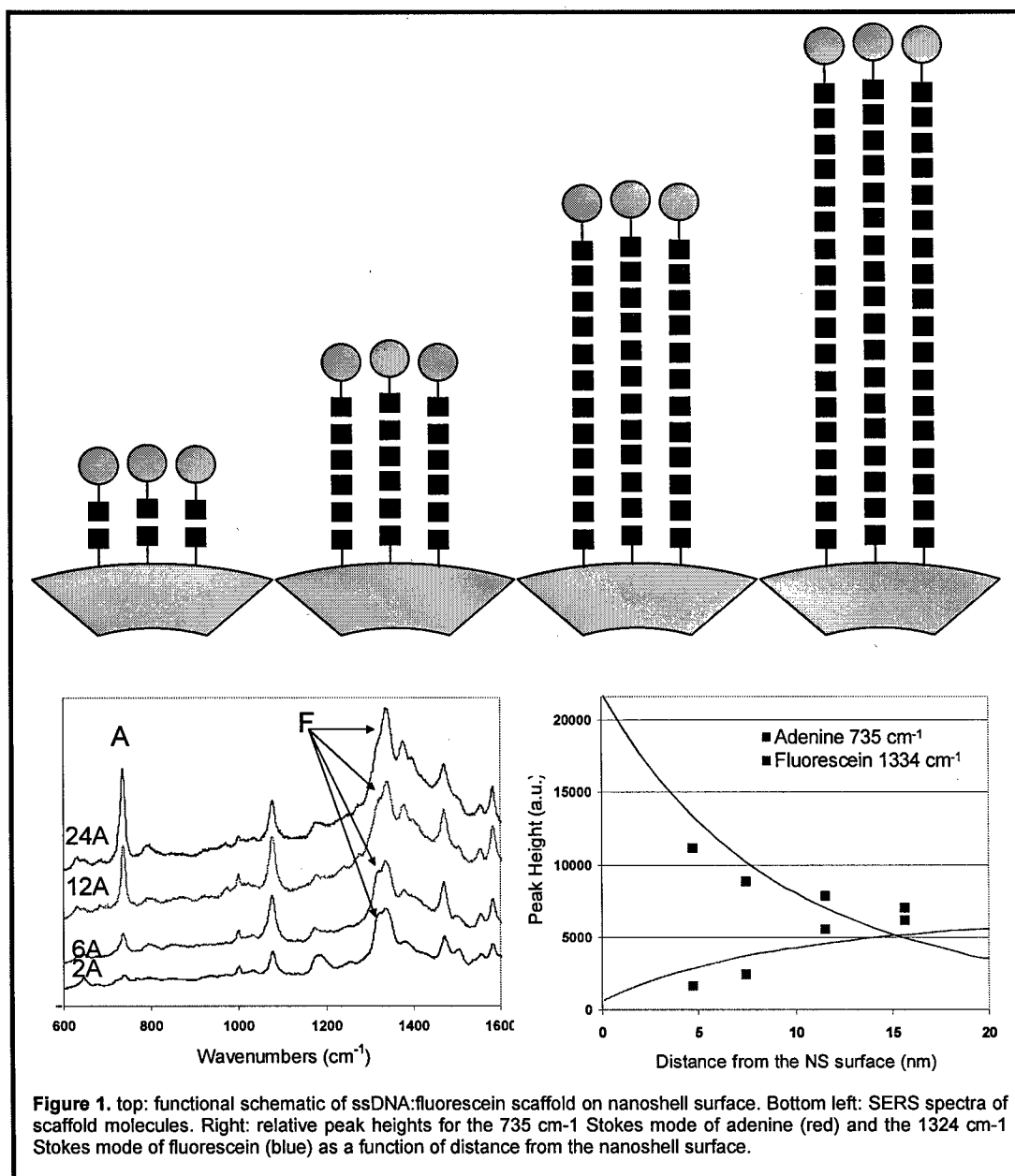
3. Status of Effort: In the third year of our research grant we have continued to make significant progress towards our stated research goals. Some of the materials systems that we have been developing were very difficult to use for studies of surface-enhanced phenomena and therefore we have streamlined our materials efforts to focus on the most robust systems for our photophysical studies. Our advancements of the past year include:

a. We have performed a comprehensive and quantitative study of the near field properties of individual nanoparticles, nanoshells, and nanoparticle and nanoshell dimers, based on confocal Raman microscopy/AFM in collaboration with the Nordlander group at Rice and the Huser group at Lawrence Livermore National Laboratory (Nano Letters 5, 11569-1574 (2005) attached);

b. We have performed a study of the interactions between a nanoparticle plasmon and the plasmons of a thin film: in this new formulation of the classical Drexhage experiment this interaction has been determined to be the electromagnetic analog of the Spinless Anderson-Fano model (Nano Letters, accepted; preprint attached);

c. We have performed a theoretical-experimental study of Cu nanoshells, where the electronic properties of Cu strongly modify the plasmon response of the nanostructure (J. Phys. Chem. B., accepted (preprint attached)).

d. The DNA based “scaffold” developed for the controlled spacing of fluorescent species near the nanoshell surface has been utilized to profile the distance dependence of the fringing, or “near” field at the nanoshell surface using surface enhanced Raman scattering (SERS), with experimental results that are in quantitative agreement with theory (manuscript in preparation);



e. We have developed a quantitative assay for molecules on a nanoparticle surface based on SERS (manuscript in preparation);

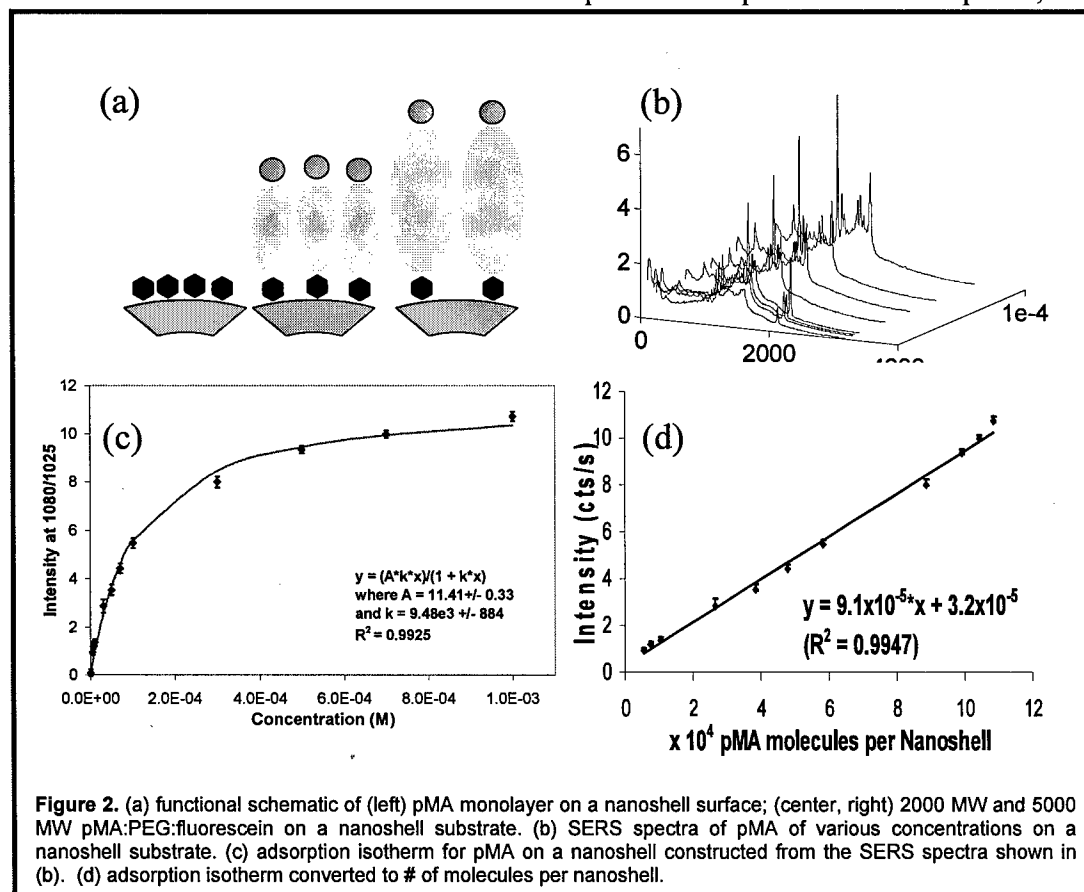
f. We have made significant progress in a study of fluorescence enhancement of the fluorophore indocyanine green near a nanoparticle surface, and have observed dependence on the plasmon energy of the nanoparticle substrates;

g. We have developed a new core-shell nanoparticle with a displaced core, that we call "Nano-eggs", and in collaboration with the Nordlander group have developed an understanding of their plasmonic properties (manuscript in preparation).

4. Accomplishments/New Findings:

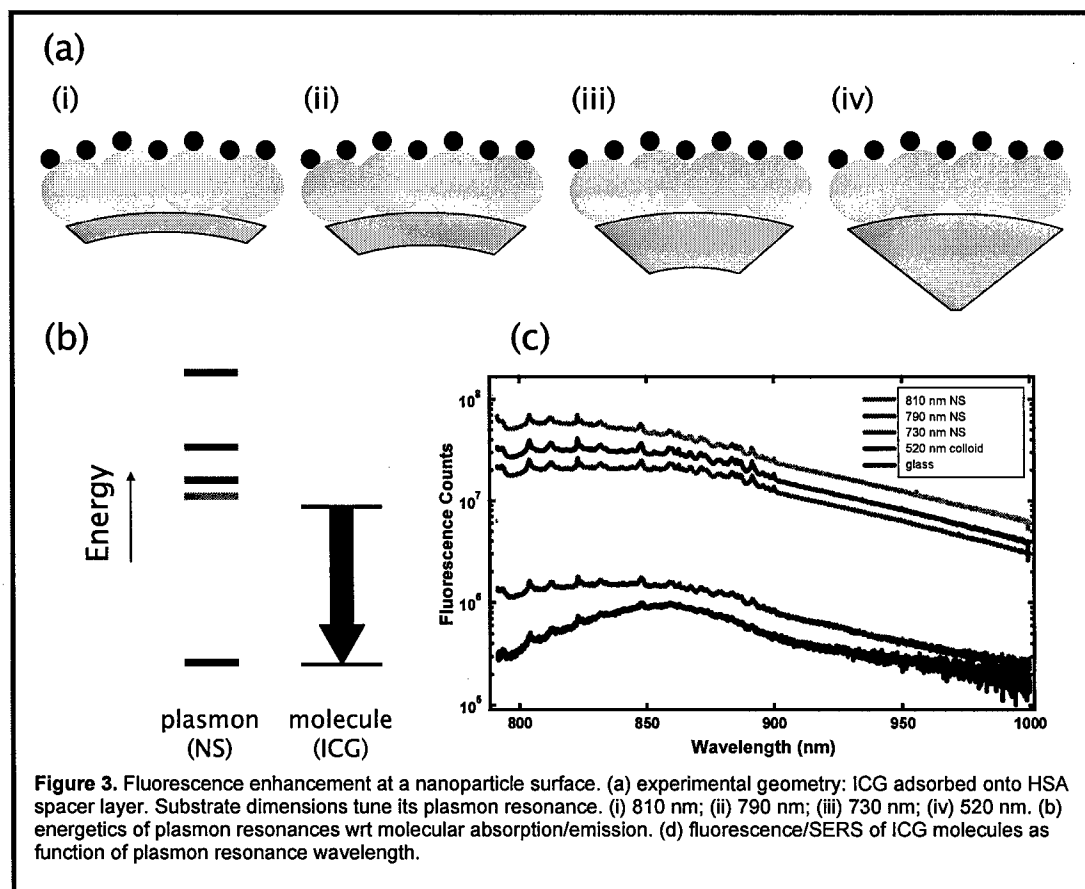
a. b. c. *See attached reprints/preprints.*

d. Nanoshell-DNA-fluorophore system: This system, originally developed for studying surface enhanced fluorescence, has proven to be an extraordinarily valuable tool for measuring the profile of the fringing field at a nanoparticle surface using SERS. A "cartoon" schematic of the molecule is shown in Figure 1. The single-stranded DNA chains are solvated in solution and are upright and extended normal to the surface of the nanoparticle. The DNA chain (poly-adenine) is terminated with a fluorescein moiety. Since both the adenines and the fluorescein provide independent Raman spectra, the



SERS spectra of a molecular layer of this complex provides distance-dependent SERS data that can be made concentration independent by normalizing the Fluorescein spectral features with respect to the adenine spectrum. The adenine and fluorescein signals as a function of distance from the surface are also shown in Figure 1. These measurements correspond quite well with the field at the positions of the adenine molecules and the fluorescein molecule obtained from theoretical calculations of the surface averaged resonant near field of the nanoparticle. This allows us to quantify the near field of a nanoparticle for the first time.

e. Quantitative assay of a molecular layer on a nanoparticle surface: The regular and reproducible SERS spectra of adsorbate molecules on nanoshells allow us to quantify the coverage of SERS-active molecules bound to a nanoshell surface (Fig. 4). Adsorption isotherms for Raman-active adsorbate molecules can be measured by exposing nanoshells to varying concentrations of adsorbates in solution. This is the first quantitative measurement technique for counting the number of molecules on a nanoparticle surface, and is uniquely dependent on the plasmon resonant properties of nanoshells that lead to a



highly reproducible SERS response. Since the SERS response of nanoshells is linear with the number of nanoparticles and independent of interparticle interactions when the nanoshell plasmon resonance is tuned to the pump laser frequency, adsorption isotherms can be performed on dilute or dense films of nanoshells deposited on a supporting

substrate. This is a general assay procedure that can be applied to any Raman-active molecular adsorbate with a binding affinity for the surface of a metallic nanoshell. We have utilized this effect to determine the number of polyethylene glycol (PEG) molecules that can be bound to a nanoshell surface. (PEG is a universally used molecule in biomedical applications that is highly effective in masking an organism's immune response, allowing any molecule or nanoparticle with a PEG attachment to remain undetected by the immune system *in vivo* for extended periods of time). In this application, PEG molecules were designed with a SERS-active benzenethiol tether for attachment to the nanoshell surface. A fluorescent tag (fluorescein) was added to this molecule to add redundancy to the assay: the paramercaptoaniline: PEG: fluorescein molecules are depicted schematically in Figure 2. Upon chemical displacement of the pMA:PEG:fluorescein molecule from the nanoshell surface, an independent quantitation using solution phase fluorescence can be performed. We have performed this assay on molecules consisting of 5000MW PEG and have determined that there are 3000 pMA:PEG:Fluorescein molecules on each nanoparticle, to a precision of approximately 20% (zeptomole sensitivity). Since PEG adsorbate molecules are capable of two structural conformations when tethered to surfaces, this assay also indicates that the PEG molecule assumes its more compact "brush" conformation (as opposed to the more expanded "mushroom" conformation) when bound to a nanoshell surface.

f. Fluorescence enhancement and the effect of plasmon resonant detuning:

By utilizing a near IR fluorophore with an emission wavelength near the nanoshell plasmon resonance, we have been able to directly and self-consistently measure plasmon-induced fluorescence enhancement as a function of plasmon resonance energy of nanoshells. These measurements were performed by using a large, protein-based spacer

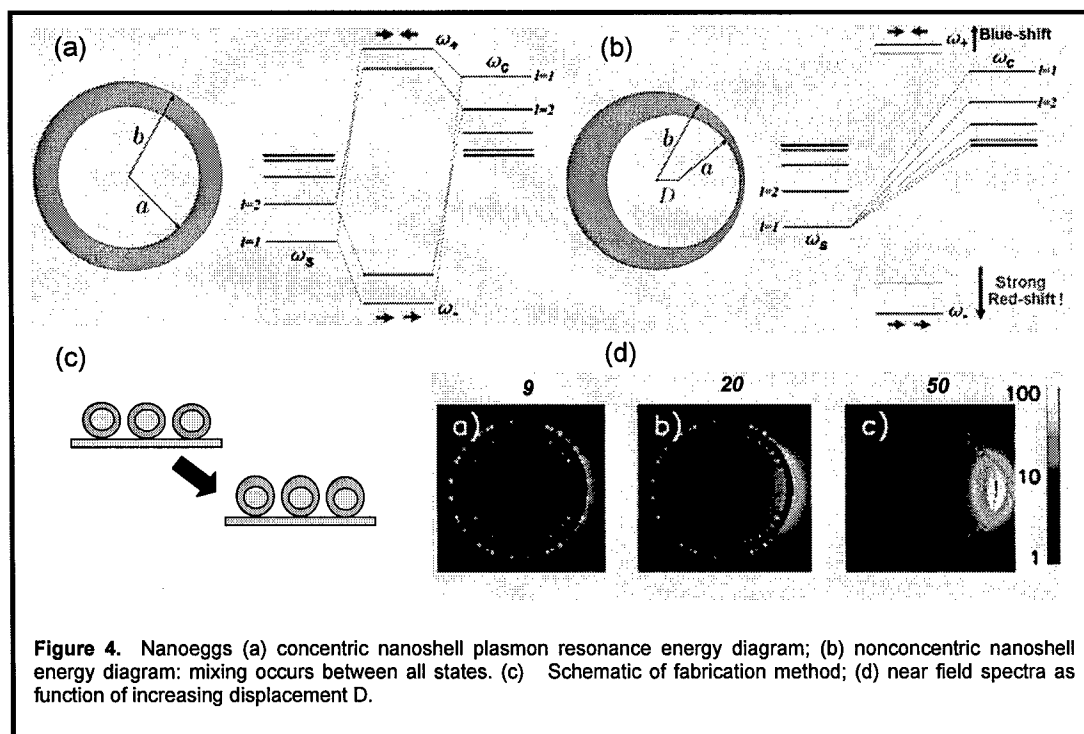


Figure 4. Nanoeggs (a) concentric nanoshell plasmon resonance energy diagram; (b) nonconcentric nanoshell energy diagram: mixing occurs between all states. (c) Schematic of fabrication method; (d) near field spectra as function of increasing displacement D .

layer (horse serum albumin, HSA) and the near-IR fluorescent molecule indocyanine green (ICG). ICG is of particular interest since it is the only FDA approved near-IR fluorophore (also known as Cardio green, it is approved in low concentrations for applications such as cardiac imaging), and because its quantum yield is low, nominally < 10%. The protein-based spacer layer is necessary to prevent the quenching of fluorescent emission at the surface of the nanoparticle. Values of fluorescence enhancement as large as 50X have been obtained from this experiment, more than 10X larger than those reported in any known nanoparticle-mediated fluorescence enhancement result to date. (This value is not inconsistent with the quantum yield of the molecule since the radiative lifetime should be appreciably reduced by the plasmon-induced enhancement, however, further quantitative studies are warranted). In a set of initial measurements the fluorescence enhancement as a function of plasmon detuning from the emission wavelength of the indocyanine fluorophore was studied. This is shown in Figure 3. This data shows strong plasmon resonance enhancement as the plasmon is tuned towards the absorption/emission wavelengths of the fluorophore. This experiment is currently being refined so that a quantitative assay of the fluorophore concentration on the nanoparticle substrate can be accurately performed.

g. Nanoshells with offset cores: Nanoeggs:

We have developed a method for fabricating nanoshells with offset cores, by reducing additional Au onto already completed nanoshells that have been deposited electrostatically onto a surface. This displaced core-shell geometry displays a strongly distorted and broadened optical spectrum. This can be understood as a mixing of the plasmon resonances of all orders with each other, resulting in a multi-peaked spectrum at the individual nanoparticle level. For example, for a very small nanoshell within the dipole limit there would be no quadrupole plasmon mode excited, however if the core and shell are displaced, as they are in the nanoegg geometry, the quadrupole mode will be excitable. Most notably, this symmetry breaking is a method for exciting the "dark" plasmon, the higher energy "anti-bonding" plasmon that has zero dipole moment for a spherical nanoparticle and thus cannot be optically excited unless symmetry is broken in this way. One potentially important aspect of Nanoeggs is that the field enhancement can be significant on the thin-metal side of the nanoparticle. This is the only known nanostructure where large enhancements can be engineered in an "open" geometry, in other words, not in the confined geometry of the junction between nanoparticles. This effect could have extremely important implications for sensor substrate development.

5. Personnel Supported:

Surbhi Lal, graduate student in Applied Physics;

Nate Grady, graduate student in Applied Physics;

Nyein Lwin, graduate student in Electrical and Computer Engineering (nanofabrication)

Britt Lassiter, graduate student in Physics.

6. Publications (all publications from last 12 months):

1. C. Aguirre, C. Moran, J. F. Young, and N. J. Halas, "Laser induced reshaping of metallodielectric nanoshells under femtosecond and nanosecond plasmon resonant illumination", *Journal of Physical Chemistry B* **108**(22) 7040-7045 (2004).
2. C. Radloff and N. J. Halas, "Plasmonic Response of Concentric Nanoshells", *Nano Letters* **4**,

- 1323-1327 (2004).
3. C. E. Moran, J. M. Steele, and N. J. Halas, "Chemical and dielectric modification of the plasmonic bandgap of metallodielectric arrays", *Nano Letters* 4, 1497-1500 (2004).
 4. Felicia Tam, Cristin Moran and N. J. Halas, "Geometrical Parameters Controlling Sensitivity of Nanoshell Surface Plasmon Resonance-based Sensors", *Journal of Physical Chemistry B* 108, 17290-17294 (2004).
 5. N. Grady, N. J. Halas and P. Nordlander, "Influence of Dielectric Function Properties on the Optical Response of Plasmon Resonant Metallic Nanoparticles", *Chemical Physics Letters* 399, 167-171 (2004).
 6. C. Nehl, N. Grady, G. P. Goodrich, F. Tam, N. J. Halas and J. H. Hafner, "Scattering Spectra of Single Au Nanoshells", *Nano Letters* 4, 2355-2359 (2004).
 7. J. B. Jackson and N. J. Halas, "Surface Enhanced Raman Scattering on tunable plasmonic nanoparticle substrates", *Proceedings of the National Academy of Sciences* 101, 17930-17935 (2004).
 8. C. Loo, A. Lowery, N. J. Halas, J. L. West, and R. Drezek, "Immunotargeted Nanoshells for Integrated Cancer Imaging and Therapy", *Nano Letters* 5, 709-711 (2005).
 9. Yu Liu, V. N. Khabashesku and N. J. Halas, "Fluorinated Nanodiamond as a wet chemistry precursor for diamond coatings covalently bonded to glass surface", *Journal of the American Chemical Society* 127(11): 3712-3713 (2005).
 10. C. Loo, L. R. Hirsch, Min-Ho Lee, E. Chang, Jennifer West, Naomi Halas, Rebekah Drezek, "Gold Nanoshell Bioconjugates for Molecular Imaging in Living Cells", *Optics Letters* 30, 1012-1014 (2005).
 11. H. Wang, G. Goodrich, Felicia Tam, Chris Oubre, P. J. Nordlander and N. J. Halas, "Controlled texturing modifies the surface topography and plasmonic properties of Au nanoshells", *Journal of Physical Chemistry B*, 109, 11083-11087 (2005).
 12. Scott R. Sershen, Glennys A. Mensing, Marie Ng, Naomi J. Halas, David J. Beebe, and Jennifer L. West, "Independent Optical Control of Microfluidic Valves Formed from Optomechanically-responsive Nanocomposite Hydrogels", *Advanced Materials*, 17, 1366-1368 (2005).
 13. Y. N. Xia and N. J. Halas, "Shape-controlled synthesis and surface plasmonic properties of metallic nanostructures", *MRS Bulletin*, 30, 338-344 (2005).
 14. Naomi J. Halas, "Playing with Plasmons: Tuning the Optical Resonant Properties of Nanoshells", *MRS Bulletin*, 30, 362-367 (2005) (invited article).
 15. Andre M. Gobin, D. Patrick O'Neal, Naomi J. Halas, Rebekah Drezek, and Jennifer L. West, "Near Infrared Laser Tissue Welding Using Nanoshells as an Exogenous Absorber", *Lasers in Surgery and Medicine*, accepted.
 16. C. E. Talley, J. B. Jackson, C. Oubre, N. Grady, T. Huser, C. Hollars, S. Lane, P. Nordlander, and N. J. Halas, "Surface Enhanced Raman Scattering from Individual Au Nanoparticles and Nanoparticle Dimer Substrates", *Nano Letters*, 5(8) 1569-1574 (2005).
 17. H. Wang, F. Tam, N. Grady and N. J. Halas, "Cu Nanoshells: effects of interband transitions on the nanoparticle plasmon resonance", *Journal of Physical Chemistry B*, accepted.
 18. F. Le, N. Lwin, J. Steele, M. Käll, N. Halas, and P. Nordlander, "Plasmons in the metallic nanoparticle-film system as a tunable impurity problem", *Nano Letters*, accepted.

7. Interactions/transitions:

- a. **Participation/Presentations at meetings, conferences, seminars, etc.:** since submission of the last progress report I have had over 45 invited talks at the locations and events listed below. In addition I have had numerous contributed talks at conferences presented by the graduate students and

postdocs (not listed, available upon request).

1. Invited talk, SPIE Annual Meeting, Denver, CO, August 2004.
2. "Biosensing Applications of Nanoshells", Becton-Dickinson, Inc., Durham, NC, September 2004.
3. Keynote Address, Chips to Hits Meeting, Boston, MA, September 2004.
4. "Truth and Beauty at the Nanoscale: Texas-Sized Molecules and Cancer Therapy", Houston Philosophical Society, September 2004.
5. "Nanoshells: New tools for manipulating light at the nanoscale", Nanotechnology Workshop, Venice, Italy, September 2004.
6. "Nanoshells: Tunable plasmonic nanostructures and applications", UC Davis, Department of Biomedical Engineering, October 2004 (postponed until 2005).
7. US-Israel Workshop in Nanoscience, Washington, DC, October 2004 (workshop postponed until 2005).
8. "SERS based Nanosensing", Air Force Review Guest Speaker, Wright-Patterson Air Force Base, November 2004.
9. AVS National Meeting, Anaheim, CA, November 2004.
10. IUMRS Meeting, Taiwan, November 2004 (declined due to conflict).
11. "Nanoshells: manipulation of light at nanoscale dimensions" NSF sponsored Nanoscience Symposium in Hong Kong, November 2004.
12. "Plasmons: Manipulation of Light at the Nanoscale", Materials Research Society Annual Fall Meeting, Boston, Mass, November 2004.
13. "Nanoshells in Biomedical Applications", U. T. M. D. Anderson Imaging Physics Research Seminar, Houston, TX, November 2004.
14. "Nanoshells: manipulating light at nanoscale dimensions for biomedicine", University of Texas Center for Biomedical Engineering Annual Conference, Westin, Galleria, Houston, TX, December 2004.
15. "Plasmonic Nanosensors", NSF-NIRT Annual Meeting, National Science Foundation, Washington, DC, December 2004.
16. "Plasmonic Nanodevices", Physics of Quantum Electronics Conference, Snowbird, UT, January 2005.
17. Fifth International Symposium on Biomimetic Materials Processing (BMMP-5), Nagoya University, Nagoya, Japan, January 2005 (declined)
18. "Nanoshells and Quantum Dots"; Featured Speaker, Saturday Night Hot Topics, Photonics West SPIE Meeting, San Jose, CA, January 2005.
19. Nanotechnology in Biomedicine, University of Bielefeld, Germany, January 2005 (declined).
20. "Nanoshells in Biomedicine", AIChE Regional Meeting, Beaumont, TX, February 2005.
21. "A Plasmonic Approach to Nanophotonics", Research Colloquium, Boston University, Boston, MA, February 2005.
22. "Nanoshells: manipulation of light at nanoscale dimensions", Harvard/MIT Physical Chemistry Seminar Series, MIT, Cambridge, MA, February 2005.
23. Distinguished Scientist Lecture Series, Trinity University, San Antonio, TX, February 21st, 2005 (physics and general lectures).
24. Invited Speaker, ACS National Meeting, March 2005.
25. Invited Speaker, IBM Almaden Research Colloquium, March 18th, 2005.
26. Invited Speaker, IEEE NDSI 2005 Meeting, Houston, TX, March 2005.
27. Invited Speaker, DARPA workshop on Nanopower, March 2005.
28. Invited Speaker, Chemistry Department, Penn State University, April 2005.

29. Invited Speaker, DOE Workshop on Single Molecule and Single Particle Spectroscopy, Gaithersburg, MD, April 2005.
30. Weissberger-Williams Lecture Series, Kodak, Rochester, NY, April 2005.
31. Invited talk, Foundations of Nanoscience Conference, Snowbird, UT, April 2005 (declined).
32. "Nanoshells: from Plasmon Physics to Cancer Therapy", NIST Colloquium Series, April 2005.
33. Invited Departmental Colloquium Speaker, Institute of Optics, University of Rochester, April 2005.
34. Invited Speaker, MRS Spring Meeting, April 2005 (two invited talks).
35. Invited Speaker, ICONO-05, St. Petersburg, Russia, May 2005 (declined).
36. Invited Speaker, Symposium in Quebec, May 2005.
37. Plenary Speaker, 13th Annual Advocacy Training Conference, National Breast Cancer Coalition Fund, Washington DC, May 2005. (could not attend due to illness)
38. Invited Speaker, Quantum Electronics and Laser Science Conference (QELS), Baltimore, May 2005. (could not attend due to illness)
39. Invited Speaker, "Minds without Borders: Frontiers in Medical Research", Medical Sciences Graduate Student Association, University of Calgary, Calgary, Alberta, Canada, May 2005.
40. Invited Speaker, Era of Hope Conference, Philadelphia, PA, June 2005.
41. Invited talk: "Plasmon Hybridization: mesoscopic quantum analogs of atomic and molecular systems", Gordon Research Conference on Atomic and Molecular Physics, June 2005.
42. Invited talk, MSS-12, Albuquerque, NM, July 2005.
43. Invited talk, Nano Summit, Houston, TX, July 2005.
44. Invited talk, DARPA workshop on Surface Enhanced Raman Scattering, San Francisco, CA, July 2005.
45. Invited talk, Gordon Research Conference on Nanoparticles and Nanocrystals, Connecticut College, July 2005.
46. Invited talk, SPIE Annual Meeting, San Diego, CA, August 2005.
47. Invited speaker, ICAVS-3 Third International Conference on Advanced Vibrational Spectroscopy, Delavan, WI, August 2005.

- b. **Consultant and advisory functions to other laboratories and agencies:** Advisory Board Member, Materials Science and Technology Division, Los Alamos National Laboratory; Advisory Board Member, Materials Research Science and Engineering Center, Penn State University

8. New Discoveries, Inventions, Patent Disclosures: to date several patents are either issued or pending on nanoshells, other nanoparticles, their process chemistry, and their applications.

9. Honors/Awards: Senior member, IEEE
 Lifetime achievements prior to this effort:
 Fellow, American Physical Society
 Fellow, Optical Society of America